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Notes:

1. Untranslatable words are replaced with asterisks (***).
2. Texts in the figures are not translated and shown as it is.

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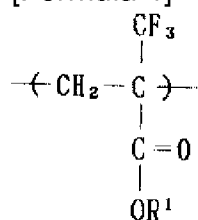
FULL CONTENTS

[Claim(s)]

[Claim 1] Resist material containing resin including the repetition unit of an acrylate system which has the substituent which has a trifluoromethyl substituent or a trifluoromethyl machine at the end, and alicycle fellows or an aromatic hydrocarbon substituent.

[Claim 2] Resist material according to claim 1 as which said acrylate system repetition unit is expressed in a bottom type.

[Formula 1]



(R1 of this formula is alicycle fellows or an aromatic hydrocarbon machine)

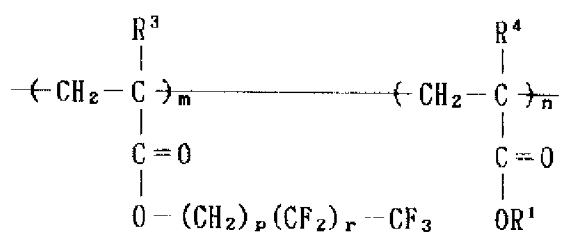
[Claim 3] Resist material according to claim 2 whose resin including said acrylate system repetition unit is an independent polymer.

[Claim 4] Resist material according to claim 2 whose resin including said acrylate system repetition unit is a copolymer.

[Claim 5] Resist material according to claim 4 obtained from the derivative with which repetition units other than said acrylate system repetition unit of said copolymer include acrylic acid, acrylic ester, and these alpha substitution objects, styrene and its derivative or vinyl ketone, and its derivative.

[Claim 6] Resist material according to claim 1 which has the structure by which said resin is shown by a bottom formula.

[Formula 2]



R¹ of this formula is alicyclic hydrocarbon or an aromatic hydrocarbon -- p -- the integer of 0-5 -- r is the integer of 0-5 and is R³. R⁴ It is the hydrocarbon group, the halogenated hydrocarbon group, hydrogen, or halogen of carbon numbers 1-4, and is R³. R⁴ You may differ, even if the same, and m and n are positive integers.

[Claim 7] Said alicyclic hydrocarbon substituent ADAMANTAN or its derivative, norbornane, or its derivative, Cyclo HEKISAN or its derivative, par hydronalium ANTORASEN, or its derivative, Par hydronalium NAFUTAREN or its derivative, tricyclo [5.2.1.0^{2,6}] Deccan, or its derivative, Resist material of any one description from Claim 1 to 6 which is the basis which makes a frame bicyclo HEKISAN or its derivative, spiro [4, 4] NONAN, its derivative, spiro [4, 5] Deccan, or its derivative.

[Claim 8] Said aromatic hydrocarbon substituent Benzene or its derivative, NAFUTAREN, or its derivative, Resist material of any one description from Claim 1 to 6 which is the basis which makes a frame ANTORASEN or its derivative, tricyclo pen TAJIEN, its derivative, FUIOREN, or its derivative.

[Claim 9] Resist material of any one description from Claim 1 to 8 which contains an AJIDO compound further.

[Claim 10] The solution of the resist material of any one description from Claim 1 to 9 is applied on a processed board. The formation method of a resist pattern including prebaking the formed resist film, exposing this resist film alternatively in radiation subsequently, and developing this resist pattern by a developing solution after forming the latent image of a predetermined pattern.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] When this invention is described in more detail about the formation method of a resist pattern of having used resist material and it, it relates to high resolving nature, high sensitivity and the positive type resist that has the outstanding dry etching tolerance, and the method of forming a resist pattern using it. This invention can offer a highly efficient resist and this resist can be used in favor of manufacture of semiconductor devices, such as Integrated Circuit Sub-Division.

[0002]

[Description of the Prior Art] as for Integrated Circuit Sub-Division, integration progresses and large scale integration circuit (LSI) and very large scale integration (VLSI) are put in practical use in recent years -- moreover, this -- the minimum pattern of an integrated circuit -- a submicron field -- and it is in the tendency to be miniaturized further from now on. Negatives are developed, after covering with a resist a processed board [in which the thin film was formed] top in formation of a detailed pattern, performing selection exposure to it and forming the latent image of a request pattern. Use of the lithography technology which obtains a desired pattern is indispensable by making a resist pattern, performing dry etching by making this into a mask, and removing a resist after that.

[0003] Although the ultraviolet-rays light of g line (wavelength of 436nm) and i line (wavelength of 365nm) is used as an exposure light source used in this lithography technology, In connection with the miniaturization of a pattern, far ultraviolet ray light with a shorter wavelength, vacuum ultraviolet-rays light, an electron beam (EB), X-rays, etc. are increasingly used as a light source. These days, the excimer laser (KrF laser with a wavelength of 248nm, ArF laser with a wavelength of 193nm) especially attracts attention as an exposure light source, and it is expected that it is effective in formation of a detailed pattern. "Radiation" In addition, on these Descriptions, when the becoming word is used, mean the light from these various light sources, i.e., ultraviolet rays, a far ultraviolet ray, vacuum ultraviolet rays, an electron beam, X-rays, various laser light, etc.

[0004] As the resist material which forms a submicron pattern using the exposure light of the vacuum ultraviolet region which is short wavelength more, For example, the polymer or copolymer of acrylic ester or alpha substitution acrylic ester which has the blocking group from which it is desorbed with an ADAMANTAN frame and acid in an ester part, The chemistry amplification type radiation photosensitive materials (refer to JP,H4-39665,A) which mix and use a photo-oxide generating agent, The polymer or copolymer of acrylic ester or alpha substitution acrylic ester which has the blocking group from which it is desorbed with a norbornane frame and acid in an ester part, There are chemistry amplification type radiation photosensitive materials (refer to JP,H5-257281,A) which mix and use a photo-oxide generating agent, chemistry amplification type radiation photosensitive materials (refer to JP,H5-257285,A) which use the mixture of the polymer of cyclohexyl maleimide or a copolymer, and a photo-oxide generating agent, etc.

[0005]

[Problem(s) to be Solved by the Invention] Such chemistry amplification type radiation photosensitivity material (chemistry amplification type resist) has attained high sensitivity and high resolving nature easily. However, the thing the acid produced from the photo-oxide generating agent is [a thing] deactivated in the interface of the resist surface and a substrate

in a chemistry amplification type resist for the alkaline substance which may exist in the substrate surface, In order to be spread into the antireflection film which may be applied on a substrate before the application of a chemistry amplification type resist, and for there to be a problem that acid concentration will fall, therefore to have applied to the real process of production of a semiconductor device, there were many required items of control like the climate control of an air ingredient, or time management. And in the conventional chemistry amplification type resist, it was required to use special equipment like climate control Caux Tarr for the climate control of an air ingredient or time management or to establish the excessive process for forming topcoat on a resist film.

[0006] This invention aims at offer of a new resist material which can form a detailed pattern especially using a short wavelength exposure light source, without troubling to climate control, time management, etc. of an air ingredient. Another purpose of this invention is to offer the method of forming a resist pattern using this new resist material.

[0007]

[Means for Solving the Problem] The resist material of this invention is the resist material containing resin including the repetition unit of an acrylate system which has the substituent which has a trifluoromethyl substituent or a trifluoromethyl machine at the end, and alicycle fellows or an aromatic hydrocarbon substituent.

[0008] The substituent which has a trifluoromethyl machine at the end can be at least in the ester of an acrylate system repetition unit by the ability of the trifluoromethyl substituent being at least in the alpha of the acrylate which constitutes a repetition unit. Alicycle fellows or the aromatic substitution machine can exist at least in the ester of an acrylate system repetition unit. When the substituent which has a trifluoromethyl machine at the end is at least in the ester of an acrylate system repetition unit, alicycle fellows or an aromatic substitution machine exists at least in the ester of a repetition unit other than this acrylate system repetition unit. Therefore, the resin which constitutes resist material serves as a copolymer of the acrylate system repetition unit which has the substituent which has a trifluoromethyl machine at the end at least in ester, and the AKURITO system repetition unit which has alicycle fellows or an aromatic substitution machine at least in ester in this case. When a trifluoromethyl substituent is at least in the alpha of the acrylate of a unit repeatedly, the resin which constitutes resist material may be an independent polymer, or may be a copolymer. [the repetition unit which forms a copolymer with the acrylate system repetition unit which has both substituents in the case of the latter] Although the unit acquired from the derivative including acrylic acid, acrylic ester, and these alpha substitution objects, styrene and its derivative or vinyl ketone, and its derivative is sufficient, it is not limited to these.

[0009] [moreover, the resist pattern formation method of this invention] The solution of the resist material of this invention is applied on a processed board, and it includes prebaking the

formed resist film, exposing this resist film alternatively in radiation subsequently, and developing this resist pattern by a developing solution after forming the latent image of a predetermined pattern.

[0010]

[Embodiment of the Invention] One mode of the resist material of this invention contains the resin which has the repetition unit expressed with the following formula (I).

[0011]

[Formula 3]



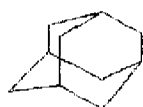
[0012] R¹ of this formula They are alicycle fellows or an aromatic hydrocarbon machine. R¹ The example of an aliphatic hydrocarbon machine expressed makes the following compounds a frame.

[0013] (1) ADAMANTAN, derivative (2) norbornane, or its derivative (3) cyclo HEKISAN, its derivative (4) par hydronalium ANTORASEN, its derivative (5) par hydronalium NAFUTAREN, or derivative (6) tricyclo [5.2.1.0^{2,6}] Deccan, its derivative (7) bicyclo HEKISAN, its derivative (8) spiro [4, 4] NONAN, its derivative (9) spiro [4, 5] Deccan, or its derivative [0014] These compounds are expressed with the following structural formula, respectively.

[0015]

[Formula 4]

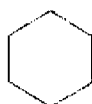
(1) アダマンタン化合物



(2) ノルボルナン化合物



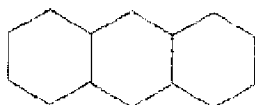
(3) シクロヘキサン



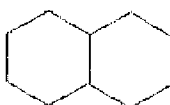
[0016]

[Formula 5]

(4) パーヒドロアントラセン



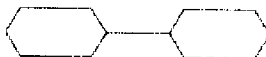
(5) パーヒドロナフタレン

(6) トリシクロ〔5. 2. 1. 0^{2,6}〕デカン

[0017]

[Formula 6]

(7) ビシクロヘキサン



(8) スピロ〔4, 4〕ノナン



(9) スピロ〔4, 5〕デカン



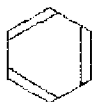
[0018] Moreover, R1 The example of an aromatic hydrocarbon machine expressed makes the following compounds a frame.

[0019] (1) Benzene, the derivative (2) NAFUTAREN, the derivative (3) ANTORASEN, its derivative (4) tricyclo pen TAJIEN, the derivative (5) FUIROREN, or its derivative [0020] These compounds are expressed with the following structural formula, respectively.

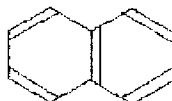
[0021]

[Formula 7]

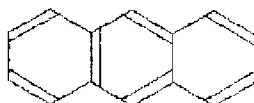
(1) ベンゼン



(2) ナフタレン



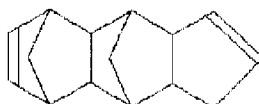
(3) アントラセン



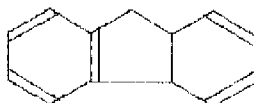
[0022]

[Formula 8]

(4) トリシクロペンタジェン



(5) フローレン



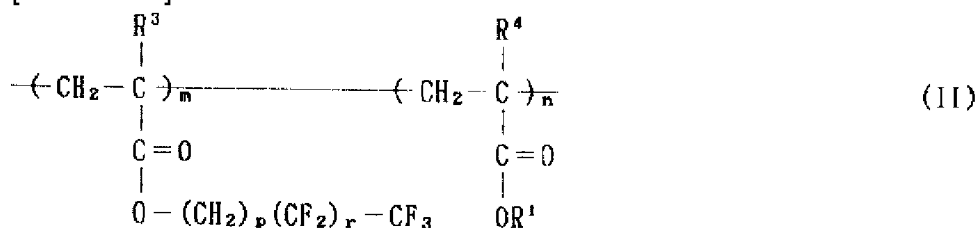
[0023] The resin which has the repetition unit of the above-mentioned formula (I) may be an independent polymer, or may be the copolymer including other repetition units. When it is resin which consists of a repetition unit of a formula (I), and another repetition unit, the another repetition unit is good in the unit acquired from the derivative including acrylic acid, acrylic ester, and these alpha substitution objects, styrene and its derivative, vinyl ketone, and its derivative, for example. In these copolymers, inside [the repetition units expressed with a formula (I) are all the repetition units] can occupy 20 to 100% preferably 5 to 100%.

[0024] Generally the weight average molecular weights of resin which have the repetition unit of a formula (I) are 2000-3,500,000. If a weight average molecular weight cannot take the dissolution rate difference to the developing solution of an exposure part and an unexposed part easily at the time of development and exceeds 3,500,000 by less than 2000, many light exposures will start making it an exposure part melt into a developing solution, and sensitivity will fall. The desirable ranges of a weight average molecular weight are 50,000-1 million.

[0025] Another mode of the resist material of this invention contains the resin which has the structure shown by the following formula (II).

[0026]

[Formula 9]



[0027] R¹ of this formula are as having defined previously and p The integer of 0-5, r is the integer of 0-5 and is R³. R⁴ It is the hydrocarbon group, the halogenated hydrocarbon machine, hydrogen, or halogen of carbon numbers 1-4, and is R³. R⁴ You may differ, even if the same, and m and n are positive integers.

[0028] Generally the weight average molecular weights of the copolymer of a formula (II) are 2000-3,500,000. If a weight average molecular weight cannot take the dissolution rate difference to the developing solution of an exposure part and an unexposed part easily at the time of development and exceeds 3,500,000 by less than 2000, many light exposures will start making it an exposure part melt into a developing solution, and sensitivity will fall. The desirable ranges of a weight average molecular weight are 50,000-1 million. Moreover, in the copolymer of a formula (II), the ratio of m:n is from 2:8 to 8:2 preferably, and is from 4:6 to 6:4 more preferably.

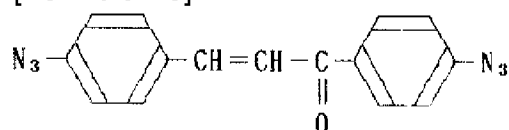
[0029] Thus, resin of the resist material of this invention is characterized by having both the substituent which has a trifluoromethyl substituent or a trifluoromethyl machine at the end, and alicycle fellows or an aromatic hydrocarbon substituent. Since a trifluoromethyl machine is electronic suction nature, when this basis exists, the electron density of the main chain of resin becomes low, therefore disassembly of a main chain takes place easilier by exposure of radiation. Even if it does not increase a light exposure from this, formation of a detailed resist pattern is attained, namely, the sensitivity of resist material becomes high. Moreover, like radiation especially the vacuum ultraviolet rays represented by ArF excimer laser light, and an electron beam, alicycle fellows or an aromatic hydrocarbon machine raises the penetration of radiation with a shorter wavelength, and also raises etching tolerance further. In this way, the resist material of this invention is high sensitivity, and it is high resolving nature and it becomes the good thing of etching tolerance.

[0030] A suitable start substance can be used for resin of the resist material of this invention, and it can prepare it easily with the technique of the usual organic synthesis so that it may be illustrated in the following work example.

[0031] The resist material of this invention can also contain an AJIDO compound as a

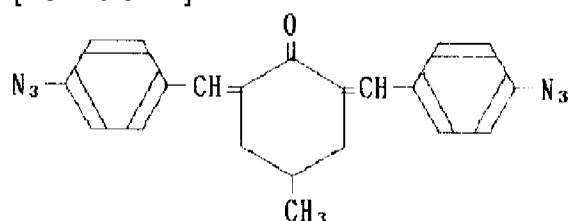
crosslinking agent. If an AJIDO compound exists, by heating, before exposing the formed resist film after applying resist material to a substrate, and stiffening resin, the molecular weight difference of resin of an exposure part and an unexposed part can be enlarged more, and it will become possible to raise sensitivity further. As an example of a suitable AJIDO compound to use it by this invention, it is 4 and 4'-diazido CULCON shown by the following formula, [0032]

[Formula 10]



[0033] 2 shown by following formula, and 6-bis(4'-horse mackerel DOBENZARU) 4-MECHIRU cyclohexa non, [0034]

[Formula 11]



[0035] ** can be mentioned.

[0036] When forming a resist pattern using the resist material of this invention, the solution of a resist is first applied on a processed board. The processed board used here may be what kind of substrate usually used in a semiconductor device and other equipment, and, specifically, can mention what prepared the oxide film, the polysilicon film, the nitriding film, the aluminum film, etc. in a silicon substrate or the surface. It is not necessary to make and these substrates do not need to be crowded, even if the circuit is already made and jammed. As for these substrates, it is desirable to pretreat with adhesion catalysts, such as hexamethyl disilazane (HMDS), for example, in order to raise adhesion nature with a resist depending on the case.

[0037] The application of resist solution can be performed using the application equipment of daily use of a spin coater, a dip coater, a roller coating machine, etc. Although the film thickness of the resist film formed can be widely changed according to factors, such as the purpose for spending of the resist film, the range of it is usually about 0.3-2.0 micrometers.

[0038] Subsequently, the formed resist film is prebaked over about 60 to 180 seconds at the temperature of about 40-230 degrees C, before exposing radiation alternatively. A heating means like a hot plate can be used for this prebaking, for example.

[0039] It exposes alternatively with the radiation of the photolithography machine of daily use of the resist film after prebaking of a resist film. Although suitable photolithography machines

are a commercial ultraviolet-rays (far ultraviolet ray and vacuum ultraviolet rays) photolithography machine, an X ray photolithography machine, electronic beam exposure equipment, an excimer stepper, and others, its exposure which makes a light source especially argon fluoride laser light or an electron beam is desirable. Exposure conditions can choose suitable conditions each time. As a result of this selection exposure, the resin itself which is the main ingredients of a resist decomposes, and the dissolution becomes possible to a developing solution.

[0040] Then, this resist film is developed by a suitable organic-solvent system developing solution according to a usual state method. As a result of development, the exposure region of a resist film carries out dissolution removal, and a resist pattern is formed. Finally, it dries according to a usual state method, and a resist pattern is obtained.

[0041] From excelling in dry etching-proof nature, when the resist material of this invention carries out dry etching of the silicon oxide film, for example with plasma, such as carbon tetrafluoride, it can perform substrate processing, using a resist pattern as a mask.

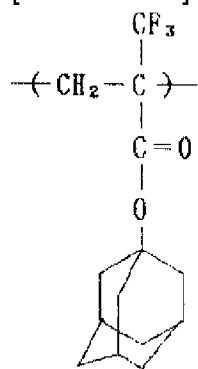
[0042]

[Example] Next, with reference to a work example, this invention is explained further. In addition, the following work example is a mere example and it cannot be overemphasized that it is not that to which this invention is limited by this.

[0043] (Work example 1) The potassium t-butoxide (0.1mol% of a monomer) of the initiator was taught to the polymerization container, and the 5-times the amount solvent tetrahydro franc of the monomer was added. - alpha-trifluoromethyl 1-adamanthyl acrylate was added into this reaction container that was 78 degrees C, after the inside of a reaction container became - 78 degrees C again, 18-crown 6 was added in equivalent amount with potassium t-butoxide, and it was made to polymerize over about 4 hours at -78 degrees C. It refined by using n-hexane as a precipitant after the conclusion of a polymerization. The alpha-trifluoromethyl 1-adamanthyl acrylate independent polymer expressed by the following formula was obtained.

[0044]

[Formula 12]



[0045] As for the obtained polymer, weight average molecular weights (Mw) are 220,000 and a

degree of dispersion. (Mw/Mn) It was 1.21.

[0046] (Work example 2) The alpha-trifluoromethyl 1-adamantyl acrylate polymer prepared in the work example 1 was dissolved in cyclohexa non. The spin coat of the obtained solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 150 degrees C on the hot plate. Selection exposure of the obtained resist film was carried out with the ArF excimer photolithography machine after completion of prebaking at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 120 seconds by Cheb Than, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. In addition, it is in that of the exposure dose in this example, and Energy Eth is 350mJ/cm². It is and the 0.25-micrometer line and space was resolved.

[0047] (Work example 3) After neglecting the sample prebaked for 100 seconds at 150 degrees C on the hot plate according to the procedure of a work example 2 in the two-week atmosphere, it was patternized like the work example 2. The obtained result was the same as the work example 2.

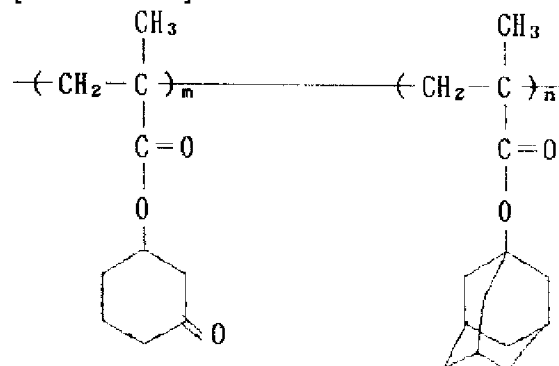
[0048] (Work example 4) The resist film was formed according to the procedure of a work example 2, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 2 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 2.

[0049] (Work example 5) The silicon substrate which prepared the organic film for antireflections in the surface was used, and it processed in the same procedure as a work example 2. Also in this case, the obtained result was the same as the work example 2 too. Skirt influence of the resist pattern which will be accepted in the case of a chemistry amplification type resist if an antireflection film is used was not observed.

[0050] (Comparative example 1) The methacrylic acid 3-oxocyclohexyl methacrylic acid adamantyl copolymer expressed with a bottom type (the m/n ratio in Mw=15,000 and a formula is 50/50)

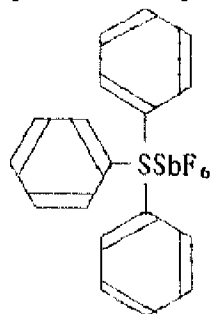
[0051]

[Formula 13]



[0052] The photo-oxide generating agent shown by a bottom formula [0053]

[Formula 14]



[0054] ** and others -- the spin coat of the chemistry amplification type resist already known was carried out so that it might become 0.7 micrometer of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 100 degrees C on the hot plate. Furthermore, the topcoat film which consists of saturated hydrocarbon resin was applied on it, and selection exposure of the resist film was carried out with the same ArF excimer photolithography machine as a previous work example at the pattern of ArF laser light with a wavelength of 193nm. Bake was carried out within 1 minute and 30 seconds for 60 seconds at 100 degrees C after exposure, and the topcoat film was exfoliated with the solvent. The resist film was developed for 120 seconds in the tetramethylbutyl ammonium hydroxide (TBAH) solution of 0.27N, and it rinsed for 30 seconds with pure water further. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. It is in that of the exposure dose in this example, and Energy Eth is 13.5mJ/cm². It is and the 0.25-line and space was resolved.

[0055] When the sample neglected without the topcoat after a resist application in the two-week atmosphere here was used, the same result as the above was not obtained and the pattern was not resolved. Moreover, after exposing immediately without applying topcoat, after applying a resist film, when it was neglected in the 2-hour atmosphere, the too same result as the above was not obtained and the pattern was not resolved. Furthermore, skirt influence was observed by the formed resist pattern when the silicon substrate which prepared the organic film for antireflections in the surface was used.

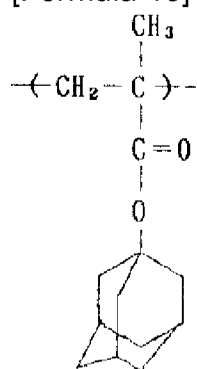
[0056] Although sensitivity is higher than the case where the resist of this invention is used when these comparative example 1 and work examples 2-5 are compared, and the conventional chemistry amplification type resist is used, it turns out that it is indispensable to make severe the climate control and time management of an air ingredient. Moreover, when an antireflection film is prepared in the substrate surface in the case of a chemistry amplification type resist, it is, If the resist of this invention is used for the resist pattern which

the acid produced from the acid generator was spread to this film, and the acid concentration in a resist film fell, therefore was formed to the phenomenon of skirt influence being accepted, it turns out that such a harmful phenomenon is not accepted.

[0057] (Comparative example 2) As shown in a bottom type, it is not a trifluoromethyl machine but a methyl group at least to alpha. 1-adamantyl methacrylate was used instead of the alpha-trifluoromethyl 1-adamantyl acrylate of a work example 1, and 1 which it has-adamantyl methacrylate independent polymer was prepared as it is also with the same way as a work example 1. The weight average molecular weight (Mw) of this polymer was 300,000, and the degree of dispersion (Mw/Mn) was 1.86.

[0058]

[Formula 15]

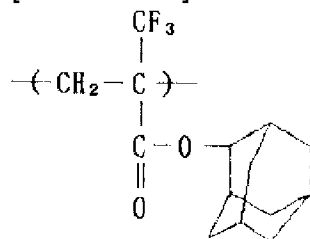


[0059] The resist pattern was formed with the same procedure as a work example 2 using this polymer. It was in that of the exposure dose in this case, and Energy Eth resolved 6800mJ/cm² and a 0.60-micrometer line and space. thus, if it is in the resist material of the acrylate resin which does not have a trifluoromethyl substituent at least in alpha, it turns out that sensitivity and resolution are boiled markedly and are inferior to the resist material of this invention.

[0060] (Work example 6) alpha-trifluoromethyl 1-adamantyl acrylate of the monomer in a work example 1 Except for having changed to alpha-trifluoromethyl 2-adamantyl acrylate, the procedure of the work example 1 was repeated and the alpha-trifluoromethyl 2-adamantyl acrylate independent polymer (Mw=200,000, Mw/Mn=1.24) expressed with the following formula was obtained.

[0061]

[Formula 16]

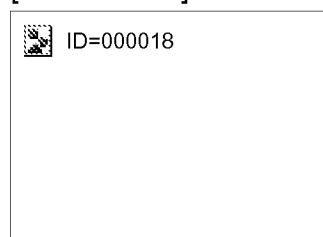


[0062] Next, work examples 2-5 were repeated using this polymer. In any case, it is in that of an exposure dose, and Energy Eth is 350mJ/cm². It is, the 0.25-micrometer line and space was resolved, and it was shown that it is the same performance as the case of work examples 2-5. Moreover, also when an antireflection film was used, skirt influence of a resist pattern was not accepted.

[0063] (Work example 7) The procedure of a work example 1 is repeated except for having changed the alpha-trifluoromethyl 1-adamanyl acrylate of the monomer in a work example 1 to alpha-trifluoromethyl 1-MECHIRU adamantyl acrylate, The alpha-trifluoromethyl 1-MECHIRU adamantyl acrylate independent polymer (Mw=310,000, Mw/Mn=1.15) expressed with the following formula was obtained.

[0064]

[Formula 17]

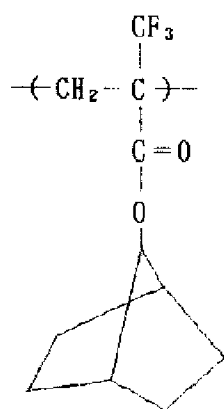


[0065] Next, work examples 2-5 were repeated using this polymer. In any case, it was in that of the exposure dose, Energy Eth resolved 350mJ/cm² and a 0.25-micrometer line and space, and it was shown that it is the same performance as the case of work examples 2-5. Moreover, also when an antireflection film was used, skirt influence of a resist pattern was not observed.

[0066] (Work example 8) The potassium t-butoxide (0.1mol% of a monomer) of the initiator was taught to the polymerization container, and the 5-times the amount solvent tetrahydro franc of the monomer was added. - alpha-trifluoromethyl norbornyl acrylate was added into this reaction container that was 78 degrees C, after the inside of a reaction container became -78 degrees C again, 18-crown 6 was added in equivalent amount with potassium t-butoxide, and it was made to polymerize over about 4 hours at -78 degrees C. It refined by using n-hexane as a precipitant after the conclusion of a polymerization. Thereby, alpha-trifluoromethyl norbornyl acrylate independent polymer expressed with the following formula was obtained.

[0067]

[Formula 18]



[0068] As for the obtained polymer, weight average molecular weights (Mw) are 250,000 and a degree of dispersion. (Mw/Mn) It was 1.27.

[0069] (Work example 9) alpha-trifluoromethyl norbornyl acrylate polymer prepared in the work example 8 was dissolved in cyclohexa non. The spin coat of the obtained solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 150 degrees C on the hot plate. having used the obtained resist film in the work example 2 after the completion of prebaking -- selection exposure was carried out with the same ArF excimer photolithography machine at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 120 seconds by Cheb Than, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. It was in that of the exposure dose in this example, and Energy Eth is 360mJ/cm2 and resolved the 0.25-micrometer line and space.

[0070] (Work example 10) After neglecting the sample prebaked for 100 seconds at 150 degrees C on the hot plate according to the procedure of a work example 9 in the two-week atmosphere, it was patternized like the work example 9. The obtained result was the same as the work example 9.

[0071] (Work example 11) The resist film was formed according to the procedure of a work example 9, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 9 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 9.

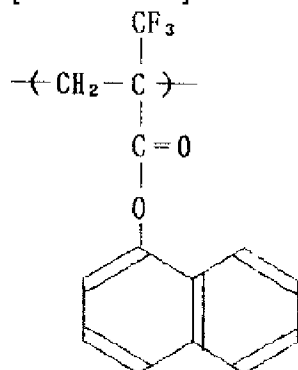
[0072] (Work example 12) According to the same procedure as a work example 9, it processed using the silicon substrate which prepared the organic film for antireflections in the surface. Also in this case, the obtained result was the same as the work example 9 too. Skirt influence of a resist pattern was not accepted, either.

[0073] (Work example 13) The potassium t-butoxide (0.1mol% of a monomer) of the initiator was taught to the polymerization container, and the 5-times the amount solvent tetrahydro franc of the monomer was added. - alpha-trifluoromethyl NAFUCHIRU acrylate was added into

this reaction container that was 78 degrees C, after the inside of a reaction container became -78 degrees C again, 18-crown 6 was added in equivalent amount with potassium t-butoxide, and it was made to polymerize over about 4 hours at -78 degrees C. It refined by using n-hexane as a precipitant after the conclusion of a polymerization. Thereby, alpha-trifluoromethyl NAFUCHIRU acrylate independent polymer expressed with the following formula was obtained.

[0074]

[Formula 19]



[0075] The weight average molecular weight (Mw) was [320,000 and the degree of dispersion (Mw/Mn) of this polymer] 1.30.

[0076] (Work example 14) alpha-trifluoromethyl NAFUCHIRU acrylate polymer prepared in the work example 13 was dissolved in cyclohexa non. The spin coat of this solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 150 degrees C on the hot plate. Selection exposure of the obtained resist film was carried out with the ArF excimer photolithography machine after completion of prebaking at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 120 seconds by Cheb Than, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. It is in that of an exposure dose and Energy Eth is 600mJ/cm². It is and the 0.25-micrometer line and space was resolved.

[0077] (Work example 15) After neglecting the sample prebaked for 100 seconds at 150 degrees C on the hot plate according to the procedure of a work example 14 in the two-week atmosphere, it was patternized like the work example 14. The obtained result was the same as the work example 14.

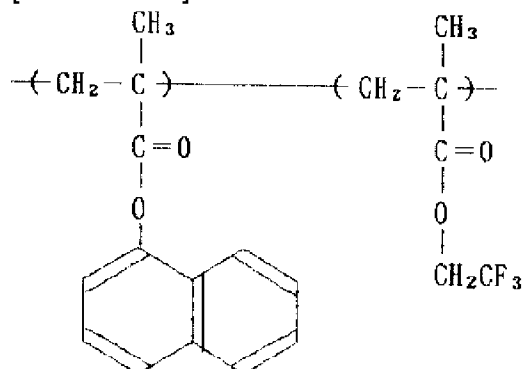
[0078] (Work example 16) The resist film was formed according to the procedure of a work example 14, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 14 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 14.

[0079] (Work example 17) The silicon substrate which prepared the organic film for antireflections in the surface was used, and it processed according to the same procedure as a work example 14. Also in this case, the obtained result was the same as the work example 14 too. Skirt influence of a resist pattern was not accepted, either.

[0080] (Work example 18) mixing NAFUCHIRU methacrylate and 2, 2, and 2-trifluoroethylmethacrylate by the molar ratio of 1:1 in a reaction container, and adding the 0.1mol initiator 2 of% of quantity of these monomers, and 2'-azobis (isobutyronitrile) (AIBN) -- and It melted in double the amount of the solvent toluene of the monomer. This system of reaction was 80 degrees C, and it was made to polymerize over about 8 hours. It refined by using n-hexane as a precipitant after the conclusion of a polymerization. The NAFUCHIRU methacrylate 2 and 2 and 2-trifluoroethylmethacrylate copolymer which are expressed by the following formula were obtained.

[0081]

[Formula 20]



[0082] The copolymerization ratio 1:1 and the weight average molecular weight (Mw) were [210,000 and the degree of dispersion (Mw/Mn) of the obtained polymer] 2.38.

[0083] (Work example 19) The NAFUCHIRU methacrylate 2 and 2 and 2-trifluoroethylmethacrylate polymer which were prepared in the work example 18 were dissolved in cyclohexa non. The spin coat of the obtained solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 150 degrees C on the hot plate. Selection exposure of the obtained resist film was carried out with the ArF excimer photolithography machine after completion of prebaking at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 120 seconds by Cheb Than, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. In addition, it is in that of the exposure dose in this example, and Energy Eth is 780mJ/cm². It is and the 0.25-micrometer line and space was resolved.

[0084] (Work example 20) After neglecting the sample prebaked for 100 seconds at 150

degrees C on the hot plate according to the procedure of a work example 19 in the two-week atmosphere, it was patternized like the work example 19. The obtained result was the same as the work example 19.

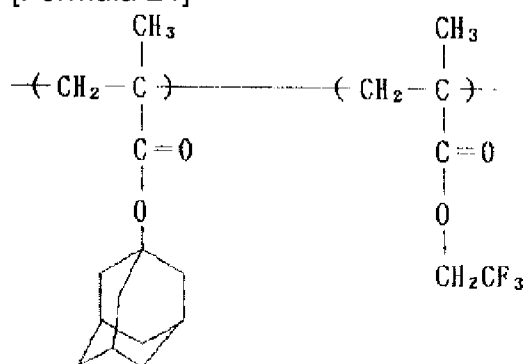
[0085] (Work example 21) The resist film was formed according to the procedure of a work example 19, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 19 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 19.

[0086] (Work example 22) The silicon substrate which prepared the organic film for antireflections in the surface was used, and it processed according to the same procedure as a work example 19. Also in this case, the obtained result was the same as the work example 19 too. Skirt influence of a resist pattern was not accepted, either.

[0087] (Work example 23) 2-adamanthyl methacrylate of the molar ratio of 1:1 and 2, 2, and 2-trifluoroethylmethacrylate were mixed in the reaction container, and AIBN of the initiator was melted in double the amount of the solvent toluene of the 0.1mol %, in addition the monomer of a monomer. This system of reaction was 80 degrees C, and it was made to polymerize over about 8 hours. It refined by using n-hexane as a precipitant after the conclusion of a polymerization. Thereby, 2-adamanthyl methacrylate 2 and 2 and 2-trifluoroethylmethacrylate copolymer which are expressed with the following formula were obtained.

[0088]

[Formula 21]



[0089] The copolymerization ratio 1:1 and the weight average molecular weight (Mw) were [240,000 and the degree of dispersion (Mw/Mn) of this polymer] 2.62.

[0090] (Work example 24) 2-adamanthyl methacrylate 2 and 2 and 2-trifluoroethylmethacrylate polymer which were prepared in the work example 23 were dissolved in cyclohexa non. The spin coat of this solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 100 seconds at 150 degrees C on the hot plate. Selection exposure of the obtained resist film was carried out with the ArF excimer photolithography machine after completion of prebaking at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 120

seconds by Cheb Than, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. It is in that of an exposure dose and Energy Eth is 720mJ/cm². It is and the 0.25-micrometer line and space was resolved.

[0091] (Work example 25) After neglecting the sample prebaked for 100 seconds at 150 degrees C on the hot plate according to the procedure of a work example 24 in the two-week atmosphere, it was patternized like the work example 24. The obtained result was the same as the work example 24.

[0092] (Work example 26) The resist film was formed according to the procedure of a work example 24, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 24 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 24.

[0093] (Work example 27) The silicon substrate which prepared the organic film for antireflections in the surface was used, and it processed according to the same procedure as a work example 24. Also in this case, the obtained result was the same as the work example 24 too. Skirt influence of a resist pattern was not accepted, either.

[0094] (Work example 28) 4 of 5weight % of the quantity of this polymer and 4'-diazido CULCON were added to 2-adamantyl methacrylate 2 and 2 and 2-trifluoroethylmethacrylate polymer which were prepared in the work example 23, and it dissolved in cyclohexa non. The spin coat of this solution was carried out by 1.0 micrometers of film thickness on the silicon substrate pretreated by hexamethyl disilazane (HMDS), and it was prebaked for 150 seconds at 200 degrees C on the hot plate. Selection exposure of the obtained resist film was carried out with the ArF excimer photolithography machine after completion of prebaking at the pattern of ArF laser light with a wavelength of 193nm. Then, the resist film was developed for 180 seconds by xylene, and the developing solution was spun off. The resist pattern of the request equivalent to the laser light pattern used for exposure was obtained without producing peeling of a pattern. It is in that of an exposure dose and Energy Eth is 80mJ/cm². It is and the 0.25-micrometer line and space was resolved.

[0095] (Work example 29) After neglecting the sample prebaked for 150 seconds at 200 degrees C on the hot plate according to the procedure of a work example 28 in the two-week atmosphere, it was patternized like the work example 28. The obtained result was the same as the work example 28.

[0096] (Work example 30) The resist film was formed according to the procedure of a work example 28, after neglecting it in the atmosphere for two days, without giving topcoat after exposure, negatives were developed like the work example 28 and the resist pattern was formed. Also in this case, the obtained result was the same as the work example 28.

[0097] (Work example 31) The silicon substrate which prepared the organic film for

antireflections in the surface was used, and it processed according to the same procedure as a work example 28. Also in this case, the obtained result was the same as the work example 28 too. Skirt influence of a resist pattern was not accepted, either.

[0098]

[Effect of the Invention] The chemistry amplification type resist material for the conventional short wavelength exposure is the sake of the climate control of an air ingredient, or time management. The resist material of this invention makes it possible to be stabilized and to form a detailed pattern, without being influenced by the neglect time and environmental atmosphere between the processes before [after applying to a substrate] development etc., in contrast with having needed use of special equipment or a film like climate control Caux Tarr or topcoat. And according to the resist pattern formation method of this invention using a resist material equipped with the characteristic which was excellent in this way, moreover, easy process control enables it to form a stable detailed pattern, without using special equipment like climate control Caux Tarr.

[Translation done.]